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WASTE FORM DEVELOPMENT FOR THE SOLIDIFICATION OF PDCF/MOX LIQUID WASTE STREAMS

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ABSTRACT

At the Savannah River Site, part of the Department of Energy's nuclear materials complex located in South Carolina, cementation has been selected as the solidification method for high-alpha and low-activity waste streams generated in the planned plutonium disposition facilities. A Waste Solidification Building (WSB) that will be used to treat and solidify three radioactive liquid waste streams generated by the Pit Disassembly and Conversion Facility) and the Mixed Oxide Fuel Fabrication Facility is in the preliminary design stage. The WSB is expected to treat a transuranic (TRU) waste stream composed primarily of americium and two low-level waste (LLW) streams. The acidic wastes will be concentrated in the WSB evaporator and neutralized in a cement head tank prior to solidification.

A series of TRU mixes were prepared to produce waste forms exhibiting a range of processing and cured properties. The LLW mixes were prepared using the premix from the preferred TRU waste form. All of the waste forms tested passed the Toxicity Characteristic Leaching Procedure. After processing in the WSB, current plans are to dispose of the solidified TRU waste at the Waste Isolation Pilot Plant in New Mexico and the solidified LLW waste at an approved low-level waste disposal facility.

INTRODUCTION

The Savannah River Site is in the preliminary design stage of the Waste Solidification Building (WSB) for the treatment and solidification of the three radioactive liquid waste streams generated by the Pit Disassembly and Conversion Facility (PDCF) and the Mixed Oxide Fuel Fabrication Facility (MFFF). The WSB is expected to treat a high alpha (TRU) waste (HAW) stream and two low alpha waste (LLW) streams. The acidic wastes will be concentrated in an evaporator and neutralized prior to solidification. Cementation has been selected as the solidification method for both the high-activity and low-activity waste streams generated in the PDCF and MFFF.

The HAW waste is a moderately acidic aqueous stream generated in the following processes: the MOX acid recovery and recycle processes; the alkaline treatment process; and the aqueous purification process. The two LLW streams consist of the stripped uranium stream (SUS), an acidic depleted uranium nitrate solution resulting from the uranium stripping process in the MFFF and, the PDCF lab liquids stream (PDCF-LL). The PDCF waste is generated from the laboratory analysis of plutonium oxide, highly enriched uranium (HEU) oxide, process samples, and waste samples. This waste also includes rinse water from equipment and drain flushes and is expected to have a pH <1.

Table 1 is the expected composition of each of the waste streams. The surrogates for the radioactive components (Am, Pu, and U) were chosen based on work by Villarreal and Spall¹.

Table 1. Composition of the Expected Waste Streams.

		HAW	SUS	PDCF-LL
Constituent	Surrogate	Average (g/L)	Maximum (g/L)	Maximum (g/L)
Am	Eu	1.21E+00	N/A	4.26E-05
Pu	Ce	8.83E-03	5.50E-03	9.34E-04
U	Ce	2.49E-01	4.00E+02 [†]	7.95E-04
Acid (M)	--	5.95E+00	2.00E+00	6.12E+00
Ga	--	2.08E+00	N/A	5.73E-05
Na	--	7.20E+00	N/A	N/A
Ag	--	1.50E+01	2.50E-01	6.10E-04
TBP	N/A	5.74E-04	1.10E-03	2.19E-03
Ba	--	8.64E-01	2.50E-01	1.47E-02
Ca	--	2.07E+01	N/A	N/A
Cd	--	1.73E-01	2.50E-01	2.50E-01*
K	--	3.80E+01	N/A	N/A
Mg	--	1.21E+01	N/A	N/A
Pb	--	3.46E-02	2.50E-01	1.13E-06
Hg	--	1.00E-02*	2.50E-01*	1.13E-02
Tl	N/A	5.00E-03*	2.50E-01*	1.13E-06
Cr	--	5.00E-02*	2.50E-01*	1.33E-02
Be	N/A	5.00E-02*	2.50E-01*	6.67E-06
SO ₃	--	N/A	N/A	8.00E-02
Cl	--	N/A	N/A	2.00E+00
F	--	N/A	N/A	2.67E-01
Acetone	N/A	N/A	N/A	1.73E-06

[†]Depleted uranium used for uranium in SUS surrogate.

*Not expected to be routinely in the waste, but included by WSB to simulate potential process upsets.

To facilitate materials handling in the proposed facility, each of the waste forms must be prepared using the same premix. The premix is the combination of cement and other materials that, when mixed with the neutralized waste, produce the solidified waste form. The water to premix ratios (w/c) for the mixes are calculated using the weight percent water in the neutralized waste solution.

OBJECTIVE

The objectives of this work are 1) To develop a waste form that will allow the HAW stream from the MFFF to be shipped to the Waste Isolation Pilot Plant (WIPP). To accomplish this objective, the waste form must be processable, contain less than one volume percent bleed water, and show evidence of gas generation rates acceptable for shipping and 2) The waste form must also be useable for the two LLW streams. The LLW waste forms must be treated

so as to be designated as non-hazardous waste for disposal in an approved low-level waste facility. Specific requirements for each of the waste forms are shown in Table 2. Other requirements/constraints such as the use of a single premix composition for all of the waste forms are listed in Table 3. The table also includes desirable properties that are not specific requirements.

Table 2. Requirements for the Three WSB Waste Forms.

	HAW	SUS-LLW	PDCF-LL
Proposed Disposal Site	WIPP	LLW disposal	LLW disposal
Requirements			
<i>Fresh/Cured Properties</i>			
No free liquid	X	X	X
Compressive strength	N/A	N/A	N/A
Set Time	N/A	N/A	N/A
Gel Time	N/A	N/A	N/A
Flowability	N/A	N/A	N/A
<i>Regulatory</i>			
Acceptable gas generation rate	X	N/A	N/A
Pass TCLP	N/A*	X	X

*Non-hazardous designation is desirable but not required.

Table 3. Additional Requirements Considered During Waste Form Development.

- One premix for all three waste forms
 - The WSB design specifies one dry materials silo to feed both the HAW and the LLW processes.
- Texture
 - The mixed waste form may be required to be either “crumbly” or self-leveling.
- Minimal or no organic processing admixtures.
- Minimize specific gravity of waste form
 - Reduce weight of waste package.
- Maximum temperature during curing <95°C.
 - Eliminate potential of steam formation during curing.
- Maximize waste loading for LLW waste forms.

DISCUSSION

Surrogate Preparation

Surrogate waste solutions of the evaporator bottoms were prepared for each of the three waste streams. The surrogates were neutralized to 1-M excess hydroxide and the weight percent solids (dissolved and undissolved) were measured. Table 4 is a summary of the measured properties of the neutralized surrogates.

Table 4. Summary of Properties of Neutralized Surrogate Waste Streams.

Property	HAW	SUS-LLW	PDCF-LL
<i>Neutralized Surrogate</i>			
Density (g/mL)	1.37	1.7	1.25
Wt. % Water	51.79	56.05	67.01
Dissolved solids (%)	43.38	24.86	32.99
Undissolved solids (%)	4.82	19.09	0.00
Viscosity (cP)	NM	16.8@ 25°C 20.3@ 66°C	NM

NM - Property not measured

HAW: To prepare the surrogate HAW waste, the composition in Table 1 was prepared from the nitrate salts, nitric acid and water. The surrogate solution omitted thallium and beryllium. Both elements are highly toxic and are underlying constituents for a hazardous designation. Therefore, if the waste form passes TCLP for the eight metals, the thallium and beryllium levels are not used for regulatory classification. The organic component, tributyl phosphate (TBP) was not added as it will not be retained by the waste form and is expected to be fully leached during the TCLP. The solution is then neutralized to 1-M hydroxide with 50 wt% sodium hydroxide solution. The amount of sodium hydroxide required is determined by calculating the amount of hydroxide necessary to neutralize the free acid, precipitate the metals as hydroxides, and attain the 1 M free hydroxide. The weight percent water was measured to be 51.79% (48.21% solids; 43.38% dissolved solids and 4.82% undissolved solids).

SUS-LLW: The surrogate for the stripped uranium stream was prepared by dissolving depleted uranium oxide in concentrated nitric acid and water to achieve a 400 g/L uranyl nitrate solution. The minor nitrate salts were then added to the solution to attain the composition for the SUS-LLW in Table 1. For this surrogate, again the thallium, beryllium and TBP were omitted. The plutonium was also omitted from this composition as it is present in small quantities and does not contribute to the value of the surrogate. The required sodium hydroxide addition was determined in the same manner as the HAW surrogate. The weight percent water of the neutralized solution was measured to be 56.05%% (43.95% solids; 24.86% dissolved solids and 19.09% undissolved solids). The density of the neutralized surrogate was measured to be 1.7 g/mL. The viscosity of the neutralized solution was measured at 25 and 66°C. The maximum viscosity at 25°C was 16.8 cP and 20.3 at 66°C.

PDCF-LL: The PDCF lab liquids waste surrogate was prepared in the same manner as the HAW surrogate. The sodium salts were used to introduce the sulfate, chloride and fluoride. The density and the weight percent solids of the acidic solution was measured ($\rho = 1.20$ g/mL; wt% solids 0.35%). The surrogate was neutralized and the weight percent water was measured to be 67.01% (32.99% solids, all dissolved).

Waste Form Development

Given that the HAW waste stream has the most restrictive requirements (see Table 2 and Table 3), and that the same premix must be used for all of the waste forms, the HAW waste

form will be developed first. The remaining waste forms will be adjusted to succeed with the premix formulation developed for the HAW waste form. A Hobart N-50 mixer was used to prepare all of the waste forms for this task.

HAW: A sample test matrix was prepared to evaluate the effects of the water to cement (premix) ratio (by mass) w/c, the addition of pozzolans*, and the use of admixtures on the processability and TCLP response of the HAW waste form. A low w/c ratio is used to minimize the free water available for radiolysis (hydrogen generation). Higher w/c ratios improve flowability of the mix and decrease the mass of the waste form (Am content is fixed in the waste, therefore less premix is required to solidify the waste form). In the range of w/c ratios evaluated in this task, the mixes prepared solely with cement as the premix material adhered to the mixing equipment. To produce a “drier” mix at the low w/c ratio, perlite, a high surface area pozzolan was added. For the higher w/c ratio mixes, a high range water reducer admixture was used to increase the flowability of the mix. Perlite is an inorganic silicate mineral. The effect of perlite on the gas generation rate is unknown. As the admixture is an organic material, there is a potential for the admixture to adversely effect the gas generation rate. However, due to the more complete mixing attained with admixture, there is also the potential for more complete reaction of the cementitious materials thus reducing the free water available for radiolysis. The admixture used in this task is Daracem 19†.

Given that most of the waste constituents form insoluble hydroxides during the neutralization process, cement alone may be sufficient to stabilize the waste. However, the waste contains significant quantities of mercury that may not be satisfactorily retained by a cement waste form. In the SRS Saltstone process, slag is used to chemically reduce the waste and stabilize/precipitate mercury. Other materials identified that can assist in the stabilization of mercury are sodium sulfide and sodium thiosulfate. In this task, slag and sodium thiosulfate were evaluated for mercury stabilization. Table 5 is a summary of the HAW mixes prepared. The neutralized waste solution used for these mixes was 52.15 wt.% water. Figure 1 is the mix #3 waste form and mixer.

Table 5. HAW Mixes Prepared.

Mix	w/c	Premix (%)	Cement (%)	Slag (%)	Perlite (%)	Waste (%)	Na ₂ S ₂ O ₃ (%)	Admixture (%)	TCLP
1	0.2	70.5	64.9	0	5.6	29.5	0	0	Y
2	0.2	70.5	32.4	32.4	5.6	29.5	0	0	Y
3	0.2	70.5	32.4	32.4	5.6	29.5	0.013	0	Y
4	0.3	61.5	30.7	30.7	0	38.5	0	0.56	Y
5	0.3	61.5	30.7	30.7	0	38.5	0.017	0.56	Y
6	0.4	54.5	27.2	27.2	0	45.5	0.02	0	N

* A siliceous material that, in a finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds having cementitious properties.

† Daracem 19, W.R. Grace



Figure 1. Mix #3. a) Mixed waste form b) uncleaned mixer blade, and c) heel remaining in mixer.

Mixes one through five were analyzed using a modified TCLP[‡]. The mixes were cured for 28 days, crushed, and pass through a 20-mesh sieve (841 μ m – 0.03 in)[§]. The crushed waste form was submitted to the Savannah River Technology Center – Analytical Development Section (SRTC-ADS) for TCLP. The resulting leachate was analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for barium, cadmium, chromium, lead, and silver and by Cold Vapor Atomic Absorption Spectroscopy (CV-AAS) for mercury. Table 6 is the concentration of these elements in the waste solution, neutralized waste solution, and the waste form for each of the mixes tested. Table 7 is a summary of the TCLP results.

Table 6. Concentration of Elements of Concern in Waste Solutions and Waste Forms.

Mix	Concentration in Waste Solution (mg/L)	Concentration in Neutralized Waste Solution (mg/L; mg/kg)	1	2	3	4	5
RCRA Element			w/c=0.2	W/c=0.2	w/c=0.2	w/c=0.3	w/c=0.3
			Concentration in Waste Form (mg/kg)				
Ba	864	571; 417	123	123	123	160	160
Cd	173	114; 83	25	25	25	32	32
Cr	50	33; 24	7.1	7.1	7.1	9.3	9.3
Pb	30	23; 17	4.9	4.9	4.9	6.4	6.4
Ag	15000	9911; 7235	2134	2134	2134	2785	2785
Hg	10	7; 5	1.4	1.4	1.4	1.9	1.9

[‡] The test was performed with 10 grams of sample rather than prescribed 100 grams. The leachant to sample ratio remained 20.

[§] The TCLP requires the sample to pass through a 3/8-inch sieve. EPA Manual SW-846, Procedure 1311.

Table 7. TCLP Results from the HAW Mixes.

Mix	TCLP	LDR [†]	1	2	3	4	5
RCRA Element	Hazardous Limit (ppm)	Treatment Limit (ppm)	Leachate concentration (mg/L)				
Ba	100	21	2.15	1.23	1.30	1.26	1.26
Cd	1	0.11	<0.014	<0.014	<0.014	<0.014	<0.014
Cr	5	0.6	0.14	<0.05	<0.05	<0.05	<0.05
Pb	5	0.75	<0.69	<0.69	<0.69	<0.69	<0.69
Ag	5	0.14	<0.3	<0.3	<0.3	<0.3	<0.3
Hg	0.2	0.025	<0.11	<0.11	<0.11	<0.11	<0.11

[†]Land Disposal Restriction limit used for treated waste already declared hazardous.

To address a concern that the silver concentration may exceed the 15 grams per liter tested, a mix with a w/c = 0.2 was prepared using a surrogate with a silver concentration of 25 grams per liter. The silver release from the TCLP was <0.3 mg/L, similar to the results for the 15 g/L silver concentration waste surrogate.

SUS-LLW: Given that mixes were prepared from the HAW surrogate that met either the crumbly or flowable condition and passed TCLP, both of the premix formulations used to produce the HAW mixes were tested with *SUS-LLW* surrogate. The constraints applied to this set of tests are as follows: The same premix formulation as the HAW must be used; the waste form must be non-hazardous (pass TCLP); and there must not be any free water after set.

To provide the customer with the option of choosing either a LLW waste form with similar processing properties to the HAW form or a processable waste form with increased waste loading, the premix formulation from Mix #3 in Table 5 was tested for both of the LLW waste forms. The goal of the first mix was to obtain a “crumbly” waste form. The neutralized *SUS-LLW* surrogate in Table 4 was mixed with the premix in a mixer using an initial w/c ratio of 0.5. The initial consistency was clayey and agglomerated into large masses. Additional premix was mixed in until the desired consistency was attained. The final calculated w/c ratio of the mix was 0.24. The second mix used the same starting materials and w/c ratio, 0.5. With continued mixing, the agglomerations developed into a homogeneous mass (on a visual scale). As the mass was repeatedly broken down and reassembled during the mixing process, the agglomerated masses began to “clean” the bowl. Figure 2 is the waste form after mixing. Table 8 is the composition of the two mixes prepared with the *SUS-LLW* surrogate. Table 9 is the TCLP results for the mix prepared with a w/c ratio of 0.5.



Figure 2. SUS-LLW mix with w/c = 0.5.

Table 8. Mixes Prepared Using the SUS-LLW Neutralized Surrogate.

Mix	w/c	Premix (%)	Cement (%)	Slag (%)	Perlite (%)	Waste (%)	Na ₂ S ₂ O ₃ (%)	Admixture (%)	TCLP
SUS-1	0.24	70.1	31.6	31.6	6.9	29.9	0.026	0	N
SUS-2	0.5	52.8	23.8	23.8	2.6	47.2	0.023	0	Y

Table 9. TCLP Results for SUS-LLW Mix with w/c Ratio = 0.5.

RCRA Element	TCLP Hazardous Limit (mg/L)	LDR [†] Treatment Limit (mg/L)	Concentration			SUS-2 Leachate Concentration (mg/L)
			Waste Solution (mg/L)	Neutralized Waste Solution (mg/L; mg/kg)	Waste Form (mg/kg)	
Ba	100	21	250	173; 102	48	0.808
Cd	1	0.11	250	173; 102	48	<0.200
Cr	5	0.6	250	173; 102	48	<0.170
Pb	5	0.75	250	173; 102	48	<2.46
Ag	5	0.14	250	173; 102	48	<0.150
Hg	0.2	0.025	250	173; 102	48	<0.11

[†]Land Disposal Restriction limit used for treated waste already declared hazardous.

PDCF-LL: Given that mixes were prepared from the HAW surrogate that met either the crumbly or flowable condition and passed TCLP, both of the premix formulations used to produce the HAW mixes were tested with PDCF-LL surrogate.

The constraints applied to this set of tests are as follows: The same premix formulation as the HAW must be used; the waste form must be non-hazardous (pass TCLP); and there must not be any free water after set.

All of the solids in the PDCF-LL neutralized surrogate were dissolved solids. To obtain a “crumbly” mix, the w/c ratio (and therefore the waste loading) would most likely be impracticably low. Therefore, the goal of this test is produce a fluid waste form. Either TCLP results or the presence of bleed water in the waste form will limit the w/c ratio (waste

loading). An initial w/c ratio of 0.4 was used with the same premix formulation from HAW mix #3. The mix was uniform and poured easily from the mixer. Table 10 is the formulation of the mix tested.

Table 11 is the concentrations of the elements of concern in the waste and waste forms as well as the TCLP results for the waste form.

Table 10. Formulation to Prepare a Waste Form with the PDCF-LL Neutralized Surrogate.

Mix	w/c	Premix (%)	Cement (%)	Slag (%)	Perlite (%)	Waste (%)	Na ₂ S ₂ O ₃ (%)	Admixture (%)	TCLP
PDCF	0.4	62.6	28.8	28.8	5	37.4	0.016	0	Y

Table 11. TCLP Results for PDCF-LL Mix with w/c Ratio = 0.4.

RCRA Element	TCLP Hazardous Limit (mg/L)	LDR [†] Treatment Limit (mg/L)	Concentration			PDCF-LL Leachate Concentration (mg/L)
			Waste Solution (mg/L)	Neutralized Waste Solution (mg/L; mg/kg)	Waste Form (mg/kg)	
Ba	100	21	14.7	11; 9	3.3	0.90
Cd	1	0.11	250	187; 149	56	<0.014
Cr	5	0.6	13.3	10; 8	3	<0.05
Pb	5	0.75	0.0011	0.0008; 0.0007	0.0003	<0.69
Ag	5	0.14	0.28	0.21; 0.17	0.06	<0.3
Hg	0.2	0.025	11.3	8.4; 6.7	2.5	<0.11

[†]Land Disposal Restriction limit used for treated waste already declared hazardous.

CONCLUSIONS

Waste forms have been prepared from surrogates of the three WSB waste streams (HAW, SUS-LLW and PDCF-LL). A mix was prepared for all three waste streams using the same premix formulation; 46% cement, 46% slag, and 8% perlite (by mass). There was no bleed water remaining in any of the waste forms after the mix had set. All of the waste forms tested have passed the Toxicity Characteristic Leaching Procedure (TCLP). The processability of the mixes will require validation after the WSB has selected a mixing system.

REFERENCES

¹ R. Villarreal and D. Spall, "Selection of Actinide Chemical Analogues for WIPP Tests," LA-13500-MS, Los Alamos National Laboratory, Los Alamos, NM August 1998.